Elaboration of highly ordered nanoporous alumina by two-step anodization: influence of experimental parameters on porous layer structure.

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Highly ordered nanoporous alumina film has been widely investigated especially since the discovery of two-step anodizing process by Masuda and Fukada in 1995 because of their possible applications in nanotechnology. Coloring, template for nanotubes and nanowire, optic and electronic nanodevices can be quoted. The geometry of these films is characterized by closed packed arrays of columnar hexagonal cells each containing a central pore. Theoretically and ideally, the cell size and the pore size are respectively comprised between 25 and 500 nm and between 10 and 300 nm. Both of them depend on the anodizing parameters. The depth of the channel is the depth of the porous layer and can reach one hundred micrometers. Practically some effort must be done concerning the study of experimental parameters influence on the porous layer structure. The aim of our work is to progress in the exhaustive study of the influence of experimental parameters. Voltage, electrolyte nature and concentration, temperature, anodizing duration, nature of the substrate and anion role have been investigated. Our aim is to be able to choose experimental parameters to obtain ordered film whatever the chosen film depth, cell size and pore size. In fact, it is well known for some geometry, a 100 nm interpore distance for instance, but less known for 150 nm for instance.

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Introduction

Since the end of 90s, elaboration of highly ordered alumina layer by anodizing is well known¹⁻⁴. If anodizing parameters are well chosen the porous alumina layer has a structure similar to a honeycomb (fig.1.a). The structure of these films is characterized by a closed packed array of columnar hexagonal cells each containing a central pore. These cells form a hexagonal network of cylindrical channels (fig.1.c), parallel each other (fig.1.b) and perpendicular to the substrate surface. The porous layer can reach some hundred micrometers and the network step can measure 25 to 300 nanometres. The geometry and the formation rate of the porous layer are controlled by many parameters^{1,2,4,5} including electrolyte temperature, voltage, anodizing time, pH and nature and concentration of the electrolyte.



Fig.1: schematic drawing of a highly ordered structure (a). SEM cross section view (b) top view (c) of a porous alumina layer formed in a 0.3 mol. L^{-1} oxalic acid at 30°C by two-step anodizing at 40V. Both anodizing were 240 min long.

There is two methods to obtain highly ordered porous alumina film: two-step anodizing⁶ and pretexturing^{2, 7, 8}. Two-step anodizing principle is to realize a first anodizing, to remove selectively the oxide layer and finally to re-anodize the same aluminum piece which has kept the memory of the first anodizing (fig.2.a). Pretexturing and two-step anodizing lead to the same structure but both methods have its advantages and its drawbacks (fig.2.b). Firstly, pretexturing allows obtaining large well-ordered area without any defect in the hexagonal organization. Theses area can reach some square centimetres⁹ whereas they are limited to some square micrometers³ in the case of two-step anodizing. Significantly larger defect-free area can't be achieved by three-step or multi-step anodizing. Secondly two-step anodizing is technically easier than pretexturing because of the surface preparation prior to anodizing. In fact, in the case of the two-step anodizing there is not nanoindentation step and a fine mechanical polishing could be sufficient because the first anodising could replace electropolishing. Finally pretexturing can only be used for small flat piece whereas two-step anodizing can be applied to big and non-flat piece. It's crucial for some possible applications.



Fig.2: schematic representation of two-step anodizing (a) and pretexturing (b).

The evolution of the nanoporous layer structure during self-ordering phenomenon was presented in our study. Then a hypothesis about the origin of mistakes in the hexagonal order was shown. In this paper, the influence of anodizing time and temperature on the formation rate of highly ordered porous alumina layer would be described. Finally the relationship between anodizing voltage, electrolyte used and cell size was considered. A new ordered regime discovered by Lee, Ji, Gösele and Nielsch was presented¹¹.

Experimental

A high purity aluminum (99.989 %) is used in this study. Aluminum is mechanically polished and electropolished for 2 min in a mixture of phosphoric acid (50 wt %), sulphuric acid (42 wt %) and aluminum sulphate (1.5 wt %) at 75°C at a constant voltage of 15 V. Anodizing have been carried out in a 10 dm³ volume cell. Compressed air is thrown through a sintered glass located at the bottom of the anodizing cell to form air micro bubbles which permit electrolyte stirring. Electrolyte temperature is maintained constant during anodizing using a cryothermostat (Fischer Bioblock 18207). An oxalic acid solution (0.3 mol.l^{-1}) is used as electrolyte for porous oxide film formation. A potentiostat (MICRONICS SYSTEMS type Microlab class MX) is used to maintain a constant voltage between the working electrode and the counter electrode. The counter electrode is made of titanium covered by an iridium oxide layer. Two-step anodizing method is used: samples are anodized, then the oxide layer is removed by immersing the sample for 60 min in a mixture of phosphoric acid (6 wt %) and chromic acid 1.8 wt %) at 60°C and finally, after chemical removal of the oxide layer, aluminum is anodized again at the same condition as used during the first anodizing. Samples are rinsed twice with water and distilled water between each step of the procedure and after the second anodizing. The surfaces of samples have been observed by scanning electron microscopy (SEM, JSM 6500 F – FEG). To realize cross sectional and bottom observations, the alumina layer is chemically separated from the aluminum substrate by immersion in a saturated HgCl₂ solution. The thickness of the oxide layer is measured on cross-sectional images.

Results and discussion

The conductivity of oxalic acid $(0.3 \text{ mole.L}^{-1})$ at 25°C is 50.2 mS.cm⁻¹. This value is quite low, then the equivalent electrolyte resistance is only about some tens ohms. This is negligible compared to the electrical résistance due to the oxide barrier layer. Thus the potential drop is mainly due to the compact barrier layer and not to the electrical resistance of the electrolyte. So the conductivity is a secondary parameter in porous anodizing.

A third inert electrode identical to the cathode was introduced in the bath. This electrode is called measuring electrode. Potential difference between anode or cathode and measuring electrode were measured before and during anodizing at 40V (fig.3). Anodic and cathodic potential related to measuring electrode are stable after about some tens seconds of anodizing and keep the same value during the anodizing. The cathodic potential related to the measuring electrode is not very modified when the potentiostat is switch on. And the initial value is recovered when the potentiostat is switch off at the end of anodizing. Whereas the anodic potential related to the measuring electrode is clearly modified when the potensitostat is switch on. This means that the potential set by the potentiostat is mainly "used" by the anodic reaction: it is used to overcome the electrical resistance of the barrier layer. The part of the potential used for the cathodic reaction is negligible. Moreover the combination of the high electrical resistance of the barrier layer and the "localization" of the potential drop in the barrier layer induce a local heating at pores base.



Fig.3: comparison of anodic and cathodic potential related to measuring electrode before anodizing and during anodizing. Anodizing were conducted in oxalic acid 0,3 mole. L^{-1} , 30°C, 40V

One-step anodizing have been done at 40V and 30°C with different durations and observed by SEM to follow the evolution of the structure with time. For short anodizing time, the alumina layer is very thin. To observe the bottom view, the alumina layer is selectively dissolved and the aluminum surface is representative of the base of the pore of the porous layer. At the beginning of anodizing, the number of cells is high, they are not hexagonal, and their size is inhomogeneous (fig.4.a). Progressively, the number of cells decreases but they become larger and tend to become increasingly hexagonal due to coalescence between cells (fig.4.a, b, c). The formation of 100 nm cells as expected^{1,6} is very fast: after only 5 min the number of cells is quite definitive but the selfordering phenomenon continues (fig.4.d). Then, after 15 minutes, some areas with perfect hexagonal order appear and will progressively grow. Nevertheless, there are still non-hexagonal cells (fig.4.e) between perfectly ordered areas, which cannot be avoided with two-step anodizing. After 40 seconds, first hexagonal cells appear at the base of the alumina layer (fig.4.b) but no hexagonal cell is observed at the top after 60 minutes. This means that the dissolution rate at the surface of alumina is quasi-zero because the alumina formed during the first 40 sec has not been dissolved after 60 min.



Fig.4: self ordering phenomenon: SEM-FEG images of the aluminum surface after dissolution of the alumina layer. One step Anodizing were conducted at 40V in a 0.3 mole. L^{-1} oxalic acid at 30°C. a) 20 sec, b) 40 sec, c) 2 min, d) 5 min, e) 15 min, f) 60 min.

In the case of two-step anodizing there are inevitably some boundaries between perfectly ordered areas (fig.5). Defects in the hexagonal order are localized on these boundaries. In fact, when the self-ordering phenomenon happens many ordered areas are formed all over the surface. Their location on the surface is random. Larger ordered areas widen over smaller area because larger areas are more stable energetically. Thus, the size of ordered areas increase and their number decreases. When two large stable areas (very stable energetically) meet, hexagonal cells of both areas are not in the same network because of their spatial orientation and position even if their shape and their size are identical (fig.5). Cells, which are located at the junction between the two networks, are distorted and form a boundary of defect in the hexagonal order.



Fig.5: SEM-FEG images of the porous layer surface. Two step anodizing was conducted at 40V in a 0.3 mole. L^{-1} oxalic acid at 30°C during 240 min and 180 min. (a) et (b). Schematic view of the defects boundary formation (c).

The specific structure of highly ordered nanoporous alumina results from the competition between the electrochemical formation of alumina and the chemical dissolution of alumina¹⁰. The thickness of the oxide layer formed at 40V at different temperatures and second step anodizing durations have been measured. Effective growth rates of the porous oxide layer are deduced from these measures (fig.6). Oxide formation rate is all the more high since the temperature is high, therefore, the effective growth rate of the alumina layer increases with temperature from 0 to 30°C to reach a maximum around 30°C. Above 30°C the dissolution phenomenon tend to become dominating what leads to a decreasing of the average effective growth rate of the oxide layer. Moreover, above 30°C the dissolution phenomenon is too effective, then, the equilibrium between the dissolution and the formation of alumina which leads to the hexagonal structure do not exist anymore. Thus, no hexagonal porous structure is observed (fig.6) because the self-ordering phenomenon of the pores could not happen anymore. So, the dissolution phenomenon must be limited and controlled by an appropriate choice of the temperature and/or the electrolyte nature and concentration to obtain highly ordered alumina porous layer.

The effective growth rate of the oxide layer decreases with time. The average effective growth rate is respectively 9.8, 5.5 and 2.5 μ m.h⁻¹ after 2, 4 and 8 hours. This phenomenon is a consequence of the evolution of the electrolyte composition at the bottom of pores (that is the place where electrochemical reactions take place) during anodizing. Inside the pores, convection does not happen and only diffusion permits homogenization of the electrolyte composition. Decreasing the concentration of oxalic acid inside the pores leads to a decrease in the anodizing current and the effective formation rate of the porous layer.



Fig.6: Evolution of the effective growth rate of the oxide layer ($\mu m.h^{-1}$), Anodizing were conducted at 40 V, in oxalic acid 0.3M at 30°C, second step anodizing duration 4 h.

Since the end of 90s, elaboration of highly ordered alumina layer by mild anodizing process is well known¹⁻⁴. In typical mild anodizing, the cell size depends linearly on the voltage ($d_{ip} = a \times V$ avec a = 2.5 nm.V⁻¹). Nevertheless the structure is highly ordered only for narrow processing conditions which correspond to well defined electrolyte / voltage couple (fig.7). If processing conditions are not exactly the defined conditions the hexagonal networks can't be formed anymore.

Acid	Concentration	Temperature	Voltage	Interpore distance
H ₂ SO ₄	2 mol.L-1	17 °C	19 V	50 nm
H ₂ SO ₄	0.3 mol.L ⁻¹	0°C	25 V	65 nm
(COOH)2	0.3 mol.L-1	0 to 30°C	40 V	100 nm
H ₃ PO ₄	1 mol.L-1	0°C	160 V	420 nm
H3PO4	0.1-0.3 mol.L ⁻¹	0°C	195 V	500 nm

*Fig.7: ideal processing conditions which lead to a hexagonal networks for «mild » anodizing*¹⁻⁶.

Lee, Ji, Gösele et Nielsch recently proposed new processing conditions which lead to highly ordered structure but with new interpore distances¹¹. It consists in high voltage anodizing in oxalic acid at 0.3 mole.L⁻¹. It is called "hard" anodizing. In the case of mild anodizing working at 40V leads to ordered structure and in the case of hard anodizing voltage from 100 to 150 V lead to ordered structure. Both structure are identical, only cell size changes (fig 8). As "mild" anodizing the cell size depend on the voltage but the proportionality coefficient is lower (2 nm.V⁻¹) in the case of "hard" anodizing. Thus cells size are between 200 and 300 nm (fig.9).



Fig.8: SEM-FEG images of the aluminum surface after dissolution of the alumina layer. One step anodizing was conducted in a 0,3 mole. L^{-1} oxalic acid at 0°C. a) 122.5V during 360 min; b) 40V during 60 min.

A comparison between "mild" anodizing and "hard" anodizing characteristics is presented in fig.9. The main innovative aspect of these new processing conditions is its high oxide growth rate comparing to "mild" anodizing. Thus, after 2 hours of anodizing, the porous layer can reach more than 100 μ m. This point is crucial so as to produce porous layer of some tens of microns.



Fig.9: comparison of "mild" anodizing process and "hard" anodizing.

Lee, Ji, Gösele et Nielsch realized their hard anodizing at $0^{\circ}C^{11}$ but we have shown that hard anodizing is also possible at room temperature (20°C) if the potential is very slowly increased from 40V to 125 V. If the potential increasing is too fast, the barrier layer is not stable anymore then the current density drastically increase and the aluminum substrate is consumed without any formation of alumina layer. "Hard" anodizing is all the more unstable, as the temperature is high. Working at room temperature is very interesting because it is not always easy to work at 0°C.

Conclusions

- 1. Thus the potential is mainly « used » to overcome the electrical resistance of the compact barrier layer. This produces an intense local heating, which enhance the dissolution phenomenon at the pore base.
- 2. The final cell size is reached after only 5 minutes during self-ordering phenomenon at the beginning of the first anodizing. Moreover boundary of defects in the hexagonal order cannot be avoided in the case of two-step anodizing.
- 3. An increasing of the bath temperature permits to increase the effective growth rate of the porous layer but above 30°C the growth rate decrease and the self-ordering phenomenon cannot happen.
- 4. Working at high potentials can also lead to ordered structures. The main advantage of this process is its high oxide layer growth rate. It also leads to structures with an interpore distance, which varies, from 200 to 300 nm. It is another noticeable advantage of "hard" anodizing because such interpore distance cannot be achieved by "mild" anodizing. "Hard" anodizing is possible at room temperature.

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